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LATTICE ENERGY OF ALKALI HALIDES

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ABSTRACT. Lattice energy of the alkali halides has been calculated by assuming the potential function in the form

$$\phi(r) = -\frac{\alpha e^2}{r} + \frac{B}{r^n} - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon_0$$

where the index n and the constant B have been determined from the equilibrium conditions and the experimental data on the compressibility and the inter-ionic distance. The values of ϕ for the alkali halides are found to be very close to the experimental values as well as to the values calculated from the exponential form of the potential function. The values of compressibility and thermal expansion are also calculated and the agreement with the experimental values is excellent.

INTRODUCTION

The theory of ionic crystals was first developed by Born and later extended by Born and Mayer (1932) and several others. The interaction energy consists of an attractive and a repulsive term in addition to the Coulomb term. The most widely used forms for the repulsive potential are an exponential variation with the distance or simply an inverse power variation. Results of quantum-mechanical calculation favour the exponential form whereas the inverse power form has the advantage of greater simplicity. The former was utilised by Born and Mayer (1932), Huggins (1937), Cubicciotti (1959) and others, but is extremely cumbersome to use. It is, therefore, worthwhile to find out whether the simpler inverse power law is equally satisfactory.

In an ionic crystal the inverse power law appears to be a good choice because there the distance between two ions does not vary widely. In fact the interionic distance will be near about that corresponding to the potential minimum. The energy per cell in an ionic crystal may be therefore represented as

$$\phi(r) = -\frac{\alpha e^2}{r} + \frac{B}{r^n} - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon_0 \qquad \ldots (1)$$

where α is the Madelung's constant, e the electronic charge, r the interionic distance and B the repulsive parameter. C represents the van der Waal attraction, D the dipole-quadropole interaction and ϵ_0 is the zero-point vibrational energy.

B and n are to be found out from the equilibrium relations (Born and Huang, 1954).

$$r\left(\frac{d\phi}{dr}\right)_{r=r_0} = -\frac{3vT}{\beta}\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P \qquad \ldots (2)$$

$$r\left(\frac{d^2\phi}{dr^2}\right)_{r=r_0} = \frac{9v}{\beta} F_{T,P} \qquad \ldots (3)$$

where

$$F_{T,P} = 1 + \frac{T}{\beta}\left(\frac{\partial \beta}{\partial T}\right)_P + \frac{T}{\beta^2 V}\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial \beta}{\partial P}\right)_T + \frac{2T}{3V}\left(\frac{\partial V}{\partial T}\right)_P$$

and β is the compressibility. If V is the molar volume, then $v = V/N = Kr^3$ in which K is a constant that is characteristic of the type of the lattice.

Recently, Sharma and Madan (1961) have assumed the value

$$\phi(r) = -\frac{\alpha e^2}{r} + \frac{B}{r^{12}} - \frac{C}{r^6}.$$

They argued that in ionic crystals the ions are of the same electronic structure as the inert gas molecules and therefore it is possible to describe a number of properties of ionic crystals with the help of Lennard-Jones (12 . 6) potential in conjunction with the Coulomb energy. They have calculated only for a few alkali halides and the results are none too satisfactory when compared with the experimental values. The assumption of the value 12 for the index is, however, open to question as Born found the value 9 to be more satisfactory with n actually varying from 6 to 12. Born, however, did not take the attraction terms involving the inverse powers 6 and 8. Therefore, we thought it desirable to include the attraction terms also in the Born expression to find out a better value of n from the experimental data and see if it is permissible to take $n = 12$ in conformity with the well-known Lennard-Jones potential

CALCULATION OF THE POTENTIAL PARAMETERS B AND n.

From (1) we can write

$$r\frac{d\phi}{dr} = -\frac{\alpha e^2}{r} - \frac{n\beta}{r^n} + \frac{6C}{r^6} + \frac{8D}{r^8} \qquad \ldots (4)$$

$$r^2\frac{d^2\phi}{dr^2} = -\frac{2\alpha e^2}{r} + \frac{n(n+1)B}{r^n} - \frac{42C}{r^6} - \frac{72D}{r^8} \qquad \ldots (5)$$

Thus combining (2) and (3) with (4) and (5) we get

$$n = \frac{\dfrac{9Kr^3}{\beta}F_{T,P} + \dfrac{2\alpha e^2}{r} + \dfrac{42C}{r^6} + \dfrac{72D}{r^8}}{\dfrac{\alpha e^2}{r} + \dfrac{6C}{r^6} + \dfrac{8D}{r^8} - \dfrac{3kr^3}{\beta}\dfrac{T}{V}\left(\dfrac{\partial V}{\partial T}\right)_P} - 1 \qquad \ldots (6)$$

$$B = \frac{r^n}{n}\left[\frac{\alpha e^2}{r} + \frac{6C}{r^6} + \frac{8D}{r^8} - \frac{3Kr^3}{\beta}\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]. \qquad \ldots (7)$$

The experimental values for the inter-ionic distances were obtained from N. B. S. Circ. (1953-1957) excepting LiI and *RbF* whose values were taken from M. L. Huggins (1937). The experimental values of compressibility were taken from *K*. Spangenberg (1956), K. Spangenberg and *S*. Hanssühl (1957) and Bridgeman 1940). Values of *C*, *D* were taken from Mayer (1933). Using these values n is found out from Eq. (6).

The values so obtained are recorded in column 3 of Table I, along with the values obtained by Born. It will be seen that the values of n now lie in a much closer range (from 6.43 to 10.66). The values for CsCl structure are seen to be higher than those for NaCl structure. Further in the NaCl structure, it increases slightly as we pass from Li to Rb, i.e., as the radius of the alkali ion increases. It also increases slightly with the increase of the radius of the halogen ion, but the increase with the positive ion radius is more marked.

CALCULATION OF THE CRYSTAL PROPERTIES

(a) *Lattice energy*

Once the parameters B and n are calculated it remains only to know the zero point energy ϵ_0. The Van der Waal's constants C and D were estimated by Mayer (1933) by careful analysis of optical data. These were tabulated by Huggins (1937). This has been calculated by Cubicciotti (1959, 1961).

TABLE I

Substance	Value of n (Born)	n from Eq. (6)	Substance	Value of n (Born)	n from Eq. (6)
Li F	6	6.43	Rb F	8 5	8.37
Cl	7	6.92	Cl	9.5	9.59
Br	7.5	7.33	Br	10.0	9.75
I	8 5	7 87	I	11.0	10 49
Na F	7	6.59	Cs F	9.5	8.96
Cl	8	8 68	Cs Cl	10.5	10.66
Br	8 5	8 60	Br	11.6	10.47
I	9.5	9.07	I	12.0	10.28
K F	8	7.79			
Cl	9	8.93			
Br	9.5	9.36			
I	10 5	9 6			

The individual terms in Eq. (1) have been calculated for $r = r_0$, the equilibrium ionic distance. These terms are summed up and recorded in Table II, along with the experimental values and also the theoretical values calculated by other workers.

It will be seen that the values obtained are almost as good as those obtained by Cubicciotti by using the exponential form which involves complicated calculations.

(b) *Crystal compressibilities*:

From the knowledge of B, n, C, D we can calculate the crystal compressibilities which can be compared with the observed values. From equation (3) we have

TABLE II

Substance		Value of n	Lattice energy in K cal/mole			
			Present work	Experimental	Calculated by Mard H	Calculated by Cubicciotti
Li	F	6 43	240.0		240 1	246 8
	Cl	6 92	198.7	198.1	199 2	202 0
	Br	7 33	188 12	189.3	188 3	190 7
	I	7.87	175 3	181.1	174 1	176 8
Na	F	6 59	217.4		213 4	218 7
	Cl	8 68	187.2	182.8	183 1	185.9
	Br	8 60	176 7	173 3	174 6	176.7
	I	9.07	164 9	166 4	163 9	164 9
K	F	7.79	194 5		189.7	194.4
	Cl	8 93	168 9	164.4	165 4	169 4
	Br	9 36	162.4	156 2	159.3	162 4
	I	9.60	152 7	151.5	150.8	153.0
Rb	F	8 37	187 2		181 4	185.9
	Cl	9 59	163 4	160.5	160 7	164.0
	Br	9 75	156 7	153 3	153 5	157.5
	I	10.49	148.9	149.0	145.3	148.7
Cs	F	8.96	178.0		173.7	178 7
Cs	Cl	10 66	156.2	155.1	152.2	155.9
	Br	10.47	150.2	148 6	146.3	151.1
	I	10.28	141.1	145.3	139.1	143 7

$$\beta = 9Kr^3F_{T,P}\Big/\Big[-\frac{2\alpha e^2}{r} + \frac{n(n+1)B}{r^n} - \frac{42C}{r^6} - \frac{72D}{r^8}\Big] \quad \ldots (8)$$

The quantity $F_{T,P}$ was calculated at $T = 298°K$. The values of β thus obtained are given in Table III along with the experimentally observed values. The agreement is excellent.

TABLE III

Substance		$F_{T,P}$ at $T=298°K$	$\beta\times10^{-12}$ Exp.	$\beta\times10^{-12}$ Calc.	$\alpha'\times10^{-5}$ Expt.	$\alpha'\times10^{-5}$ Calc.
Li	F	9899	1 43	1 43	9 2	9.18
	Cl	8843	3.17	3 14	12 2	12.24
	Br	8803	3 90	3 90	14.0	14 00
	I	9192	5.3	5 30	16.7	16 7
Na	F	.824	2 06	2.05	9 8	9 956
	Cl	1 0332	3.97	3 97	11.0	11 01
	Br	9591	4 75	4 75	11 9	11.88
	I	9949	6 21	6 35	13.5	13.56
K	F	.8897	3 14	3 14	10 0	10.0
	Cl	9601	5.50	5 39	10 1	9.93
	Br	1.0074	6.45	6.45	11 0	11.07
	I	.9784	8 07	8.06	12 5	12 00
Rb	F	.9470	3.66	3.66	9 5	9 5
	Cl	1 028	6.16	6.16	9.85	9.57
	Br	1.0457	7.38	7.31	10 4	9.81
	I	1.0786	9.00	9.00	11.9	11 14
Cs	F	.9443	4.25	4.25	9.5	9.49
	Cl	1 0078	5 55	5.55	13.65	13.65
	Br	9568	6 28	6.30	13.9	13 97
	I	1.0062	7.83	7 83	14.6	16.27

(c) *Thermal expansion*

The thermal expansion can also be calculated and compared with the experimental values. Dividing (2) by (3) and using (4) and (5) we obtain for the coefficient of thermal expansion α' the relation

$$\alpha' = \frac{3F_{T,P}}{T}\left[\frac{\frac{\alpha e^2}{r} - \frac{nB}{r^n} + \frac{6c}{r^6} + \frac{8D}{r^8}}{\frac{2\alpha e^2}{r} + \frac{n(n+1)B}{r^n} - \frac{42C}{r^6} - \frac{72D}{r^8}}\right] \quad \ldots (9)$$

The values of α' calculated from (9) are given in Table III along with the experimental values. The agreement with the experimental values is again quite satisfactory, except in the case of CsI where probably some of the experimental data utilised are in error.

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